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Hydrocarbon source apportionment for the 1996 Paso del Norte Ozone Study

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Abstract

The 1996 Paso del Norte (PdN) ozone study was conducted to improve current understanding of the significant meteorological and air quality processes that lead to high concentrations of ozone in El Paso, Texas (USA) and Ciudad Juárez, Chihuahua (Mexico). Two-hour canister samples were collected five times daily at 05.00–07.00 h, 07.00–09.00 h, 09.00–11.00 h, 11.00–13.00 h, and 15.00–17.00 h MST during intensive study periods at one urban and one rural site on each side of the border. An automated gas chromatograph was operated at one site in central El Paso. Source profiles (the fractional chemical composition of emissions) from motor vehicles, gasoline, liquefied petroleum gas, and commercial natural gas were combined with source profiles from other studies for input to the Chemical Mass Balance (CMB) receptor model to apportion the measured non-methane hydrocarbons (NMHC) to sources. On-road vehicle emissions accounted for one-half to two-thirds of the NMHC in Ciudad Juárez and El Paso with the highest contributions occurring during the morning and afternoon commute periods. Emissions from diesel exhaust contributed approximately 2–3% of NMHC in Ciudad Juárez and less than 2% in El Paso. The average sum of liquid gasoline and gasoline vapor increased during the day in Ciudad Juárez from 2% at 06.00 h to approximately 12% at 16.00 h. Diurnal and day-of-the-week patterns in the liquid gasoline contributions are essentially identical to the corresponding patterns for motor vehicle exhaust, which suggest that a large fraction of the liquid gasoline contribution may be associated with tailpipe emissions rather than evaporative emissions from motor vehicles or industrial sources. Including the sum of the two sources put the upper limit for tailpipe contributions at 60–70% of NMHC.

Keywords: Volatile organic compounds; Hydrocarbons; Ozone precursors; Source apportionment

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1. Introduction

The El Paso and Sunland Park areas of west Texas and the adjoining city of Ciudad Juárez, Mexico (Paso del Norte region) exceed U.S. and Mexican ambient air quality standards for ozone. The 1996 Paso del Norte (PdN) ozone study was conducted as part of a continuing co-operative U.S.–Mexico effort to develop understanding of the significant meteorological and air quality processes that lead to high concentrations of ozone in the Paso del Norte region. Roberts et al. (1997) and MacDonald et al. (2001) provide a summary of the background, objectives, and field measurement program for the Paso Del Norte study, and the data analyses that were carried out as part of the study.

The measurements performed during the 1996 Paso del Norte ozone study include continuous monitoring of surface and aloft air quality and meteorological conditions. The field program also included non-continuous measurements of surface and aloft air quality during selected intensive operations period (IOP) days. IOP days were selected by forecasting for high ozone concentrations during the period from 8/3/96 to 9/21/96. Routine surface meteorological and air quality data were obtained from the Aerometric Information Retrieval System, Texas Natural Resource Conservation Commission (TNRCC), Los Alamos National Laboratory (LANL), New Mexico Environment Department, Western Regional Climate Center, El Paso City County Health and Environment Department, AeroVironment (AV), and Sonoma Technology, Inc. Surface hydrocarbon and carbonyl data were collected during the field program at 12 of the 19 air quality/meteorological monitoring sites.

The chemical mass balance receptor model was applied to the ambient hydrocarbon data from the PdN ozone study to apportion ambient NMHC to emission sources and provide an independent evaluation of the relative contributions of sources to ambient levels of ozone precursors in the PdN study area. The source apportionment results obtained from this study are presented in this paper.

2. Methods

2.1. Collection of ambient hydrocarbon samples

Surface hydrocarbon and carbonyl data were collected during the field program at 12 of the 19 air quality/meteorological monitoring sites. Routine hydrocarbon samples were collected at three of these sites as part of existing continuous air monitoring station (CAMS) network operations operated by TNRCC. Canister samples were collected on a 6-day schedule at El Paso CAMS 12 (University of Texas at El Paso-UTEP) and El Paso CAMS 30 (Ascarate Park). An automated gas chromatography system (auto-GC) was operated by the TNRCC at the Chamizal Park site with speciated hydrocarbon data reported hourly. Canister samples were also collected by AV and LANL at four sites concurrent with IOP measurements (Winn Road, Turf Road, 20/30 Club, and El Paso CAMS 6-Campbell) and at five sites as part of a special hydrocarbon survey (El Paso CAMS 30-Ascarate Park, Sunland Park, Zenco, Franklin Mountain, and Dyer Street). For IOP sampling, 2-h samples were collected 5 times daily at 05.00–07.00 h, 07.00–09.00 h, 09.00–11.00 h, 11.00–13.00 h, and 15.00–17.00 h MST. For the hydrocarbon survey, 2-h samples were collected twice daily at various times. During IOPs, AV also collected 2-h carbonyl samples concurrently with the canister samples at two surface air quality sites (Turf Road and Winn Road). Similar 2-h samples were collected at the 20/30 Club during IOPs after 9/5/96 by LANL. Fig. 1 shows the locations of the ten ambient monitoring sites for which CMB analyses were performed, and Fig. 2 shows the mean wind frequencies by direction and speed at El Paso. Additional details on sampling methodologies used in this study are presented in Roberts et al. (1997) and MacDonald et al. (2001).

Hydrocarbon canister samples were collected in polished stainless steel canisters. Of the 189 canisters collected during the study, 89 samples were analyzed at the Desert Research Institute in Reno, NV (Zielinska, 1996), the National Exposure Research Laboratory of the U.S. Environ-

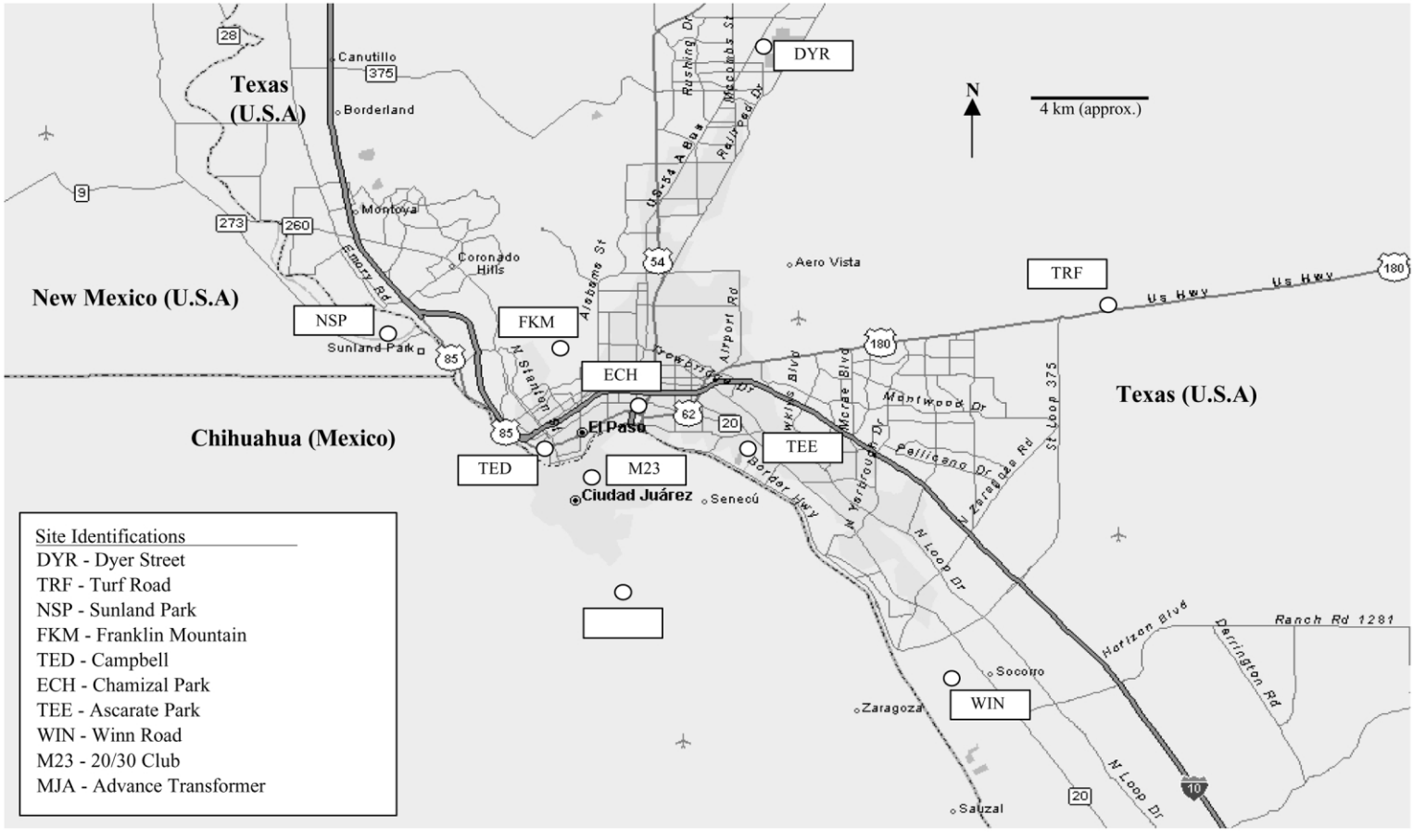

Fig. 1. Locations of hydrocarbon sampling sites for which CMB analyses were performed during the 1996 Paso del Norte ozone study. Darker shaded areas are developed regions in El Paso and Ciudad Juárez.

mental Protection Agency (EPA) in Research Triangle Park, NC analyzed 61. The University of Texas at Austin analyzed 26, and 13 were not analyzed due to canister or sampling problems. Hydrocarbon results for 54 samples collected at the 20/30 Club and Advance Transformer were

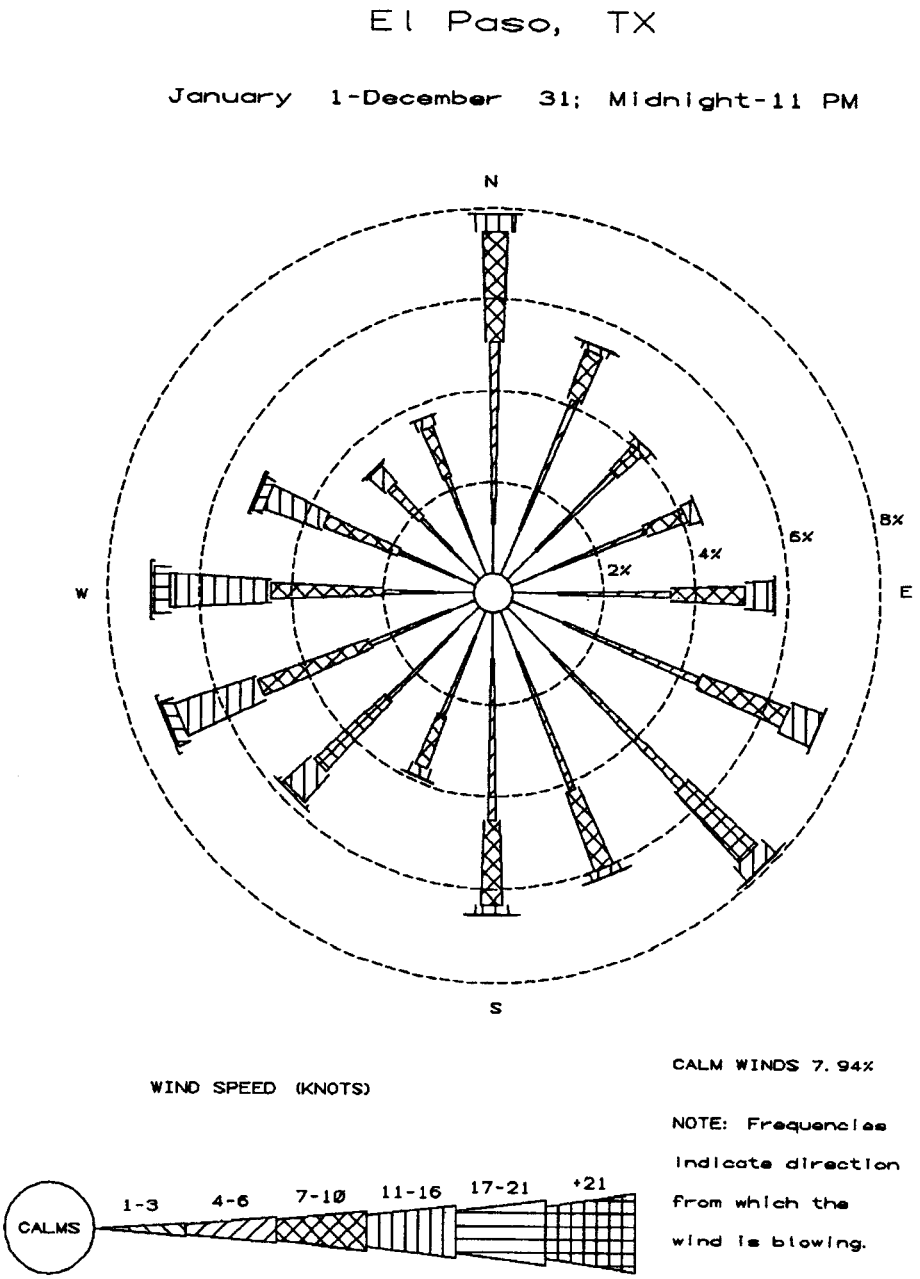

Fig. 2. Mean frequencies of wind direction and speed (1984–1992) at El Paso, Texas airport.

also received from the Instituto del Petroleo Mexicano. Roberts et al. (1997) lists the species reported by each of the five laboratories.

2.2. Collection of source samples

Source composition profiles were derived from source-specific samples that were collected during the study and analyzed at the EPA (Seila et al., 2000). Samples were collected in Ciudad Juárez near a heavily traveled intersection during rush hour and behind a propane bus in order to obtain approximate source composition profiles for 'on-road vehicle emissions' and a propane-powered bus, respectively. The average ratios between these two profiles for larger hydrocarbons were used to subtract the contribution of the Ciudad Juárez traffic from the propane bus profile. The vehicle emissions profile from Ciudad Juárez contains a mixture of exhaust emissions from gasoline-, diesel-, and propane-powered vehicles. It may also reflect contributions from running evaporative emissions and regional background. Vehicle emissions from El Paso were not collected.

Other source samples that were collected during the study include two liquefied petroleum gas samples from both El Paso and Ciudad Juárez, and one natural gas sample from Ciudad Juárez. Hydrocarbon samples from industrial sources were collected between 8/6/96 and 8/17/96 at several source-specific locations described as Chevron Tank, Chevron Tank South, Chevron Tank FCC, Delmex (ITT), Delmex downwind, Zenco, and Paint Shop. The first three sites are intended to represent fugitive VOC emissions from refinery operations. Delmex and Zenco are located in the industrial area of Ciudad Juárez, and the paint operation is an auto body shop. A diesel exhaust profile developed by Sagebiel et al. (1996) from the Ft. McHenry Tunnel in Baltimore, Maryland (USA), was also used in the apportionment.

Analyses by Consolidated Sciences, Inc. of different brands and grades of gasoline from the El Paso/Ciudad Juárez area were used to derive composite liquid gasoline profiles. Three alternative composite profiles were derived for Mexican gasoline based on weighting of regular and premium grades of 50:50, 67:33, and 75:25. The composite for the gasoline sold in El Paso is based on average relative sales in the U.S. of regular (68%), mid-grade (12%), and premium (20%) grades. Because headspace vapors were not analyzed in the study, available vapor profiles for leaded and unleaded gasoline from Mexico City were used (Mugica et al. 1998).

A large variety of formulations are used in surface coatings, and it is unlikely that one or two profiles adequately represent the emissions from all surface coatings. The most recent data are those of Censullo et al., (1996). Eleven categories of coatings were analyzed in this study. Species profiles were obtained for 106 samples of water- and solvent-based coating samples. Surface coating profiles for solvent-based industrial maintenance coatings, solvent-based medium gloss/high gloss, solvent-based primers and sealers, quick-dry primers and enamels, and thinning solvent were evaluated in the apportionments. Isoprene was used as a single-component biogenic profile.

2.3. Chemical analysis of ambient and source samples

For this project, NMHC consists of C2–C11 hydrocarbons (up to undecane) measured by gas chromatography with flame ionization detection (FID) (EPA Method TO-14A, U.S. EPA, 1997). Compounds other than the 55 Photochemical Assessment Monitoring Station (PAMS) target NMHCs that were identified by the various laboratories were grouped into a category named 'others'. Compounds reported as 'unknown' were grouped into a category named 'unidentified'. Sums of 'other' and 'unidentified' compounds were derived for the source-oriented and other canister-based ambient samples. However, the sum of 'others' could not be determined with the auto-GC data as only the PAMS target species and total NMHC were reported. The differences between NMHC and the sum of the PAMS species are reported here as 'unidentified' for the auto-GC data. In addition to other compounds, the auto-GC 'unidentified' may include decane and undecane, which are PAMS target compounds that were not reported in the auto-GC database.

The NMHCs that are not assigned to individual identified species in the gas chromatographic analysis were combined in the profile 'unidentified' (unid). A single constituent source profile consisting of 100% unidentified compounds has been used in the past to account for the contributions from this component and was also applied here. Higher contributions of unidentified compounds are typically found in downwind samples due to greater amounts of oxidized organic compounds. The 'unexplained' source contributions in this paper refer to the differences between the measured NMHC and the sum of the predicted contributions of identified source categories including unidentified compounds. The species 'unidentified', decane, and undecane were not used as a fitting species in the CMB analysis of the auto-GC data due to the incompatibility between source and auto-GC ambient data. The categories 'unexplained' and 'unid' are apportioned separately for the canister ambient data, but are combined in the apportionment of the auto-GC data. Also, the apportionments of diesel exhaust are less reliable in the apportionment of the auto-GC data due to missing data for decane and undecane.

2.4. Source apportionment

The CMB8 receptor model (Watson et al., 1998) was applied to 42 samples from 20/30 Club (M23), 50 samples from Advance Transformer (MJA), 7 samples from the Ciudad Juárez Police Station (JPS), 44 samples from Campbell (TED), 8 samples from Franklin Mountain (FKM), 9 samples from Ascarate Park (TEE), 10 samples from Sunland Park (NSP), 9 samples from Dyer Street (DYR), 33 samples from Winn Road (WIN), and 36 samples from Turf Road (TRF). CMB8 was also applied to 2232 auto-GC hydrocarbon samples from Chamizal Park in El Paso covering a period from 6/1/96 to 9/30/96. The default set of profiles used for canister samples was also used for the auto-GC hydrocarbon data.

A subset of the ambient samples were apportioned using alternative sets of source profiles listed in Table 1 in order to test for collinearity among source profiles and to select a default set of source profiles. The profiles include heavy-duty diesel exhaust from the Ft. McHenry Tunnel (Tu–MchHD), 'vehicle emissions' (Ciudad Juárez rush hour traffic, Exh–J), composite liquid gasoline weighted by a 75:25 ratio of regular and premium Mexican gasoline (ME75R25P), composite gasoline headspace vapor (Maga–HS), liquefied petroleum gas (LPG) sold in Ciudad Juárez (Prop–J), commercial natural gas sold in Ciudad Juárez (CNG–J), a composite of surface coatings (COATcomp), isoprene emissions (Biogenic), and unidentified (unid). Additional source profiles that were evaluated and results of sensitivity tests are described by Fujita (1998). The adjusted propane bus exhaust profile (Exh–PBa) and the two industrial source profiles were collinear with the above profiles and were not included in the default set of profiles.

The profiles used in CMB8 were expressed as volume percentages and are normalized to the sum of the 55 PAMS target hydrocarbons (see Table 1). The PAMS species typically account for 70–80% of the total ambient hydrocarbons in urban locations, and are more reproducible among different laboratories than total NMHC. One-sigma uncertainties were derived from variations among multiple measurements for a particular source type or a nominal analytical uncertainty of 15% was used. The assigned uncertainties are the larger of the two values. As an aside, the source profiles measured in the study area and used in the CMB analyses are presented elsewhere (Seila et al., 2000) as a percentage of the total NMHC (percentage of detected hydrocarbons); these include the vehicle emission, propane bus exhaust, LPG, and CNG profiles from Ciudad Juárez.

For the CMB calculations performed in this study, only species with summertime lifetimes greater than that of toluene ($\sim$ 9 h) were used as fitting species (see footnote b in Table 1). Despite its reactivity, isoprene was included as a fitting species because it serves as a marker for biogenic emissions. Thus, the source contribution estimates underestimate the actual source contributions of biogenic emissions, i.e. they provide a lower limit to biogenic contributions.

Table 1
Source profiles applied in the Paso del Norte Ozone Study (volume percent of sum of 55 PAMS target species)[a] MS target species)[a]

PROFILE		Juarez Vehicle Emissions (Exh_J)	Diesel Exhaust (Tu_MchHD)	Adjusted Propane Bus (Exh_Pba)	Liquid Gasoline (ME75R25P)	Gasoline Vapor (Maga_HS)	Liquefied Petroleum Gas (Prop_J)	Commercial Natural Gas (CNG_J)	Industrial (ChevFC)	Industrial (Zenco)	Surface Coating (COATcomp)
ethene		5.19 ± 0.78	9.87 ± 2.81	6.30 ± 0.95	0.00 ± 0.13	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	2.34 ± 0.35	2.65 ± 0.96	0.00 ± 0.44
ethane	*	0.95 ± 0.14	1.18 ± 0.68	2.08 ± 0.51	0.00 ± 0.13	0.00 ± 0.12	1.51 ± 0.30	78.06 ± 11.72	22.80 ± 14.90	9.98 ± 1.51	0.00 ± 0.44
acetylene	*	5.29 ± 1.47	2.55 ± 1.71	3.72 ± 0.65	0.00 ± 0.13	0.17 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.41 ± 0.20	3.07 ± 1.38	0.00 ± 0.44
Propene		2.00 ± 0.73	3.99 ± 0.93	5.01 ± 2.39	0.00 ± 0.13	0.11 ± 0.12	0.13 ± 0.21	0.00 ± 0.20	3.30 ± 1.40	0.98 ± 0.23	0.00 ± 0.44
n-propane	*	3.06 ± 0.46	2.22 ± 1.05	57.90 ± 8.69	0.02 ± 0.01	1.44 ± 0.19	85.60 ± 12.86	15.75 ± 2.37	21.50 ± 3.24	21.49 ± 3.24	0.00 ± 0.44
isobutane	*	0.86 ± 0.13	0.27 ± 0.29	3.53 ± 1.74	0.53 ± 0.15	4.80 ± 0.50	2.47 ± 0.42	2.26 ± 0.39	4.27 ± 1.13	3.51 ± 2.20	0.00 ± 0.44
1-butene		0.00 ± 0.20	2.95 ± 0.55	0.00 ± 0.20	0.00 ± 0.01	0.06 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	1.05 ± 0.25	0.45 ± 0.13	0.00 ± 0.44
n-butane	*	3.72 ± 0.56	0.64 ± 1.58	17.77 ± 10.14	2.52 ± 0.60	19.82 ± 1.99	9.58 ± 4.71	3.76 ± 0.60	11.33 ± 6.42	3.54 ± 0.68	0.00 ± 0.44
t-2-Butene		0.96 ± 0.43	0.24 ± 0.44	1.65 ± 2.34	0.04 ± 0.01	2.19 ± 0.25	0.00 ± 0.20	0.00 ± 0.20	0.31 ± 0.12	0.09 ± 0.11	0.00 ± 0.44
c-2-butene		0.30 ± 0.05	0.29 ± 0.11	0.06 ± 0.01	0.01 ± 0.01	1.91 ± 0.23	0.00 ± 0.20	0.00 ± 0.20	0.28 ± 0.06	0.56 ± 0.79	0.00 ± 0.44
isopentane	*	8.80 ± 1.32	1.31 ± 3.43	0.57 ± 0.28	5.92 ± 1.57	36.40 ± 3.64	0.34 ± 0.21	1.30 ± 0.28	3.54 ± 1.14	3.41 ± 0.88	0.00 ± 0.00
1-pentene		0.42 ± 0.06	0.89 ± 0.21	0.05 ± 0.01	0.28 ± 0.07	0.98 ± 0.16	0.00 ± 0.20	0.00 ± 0.20	0.43 ± 0.29	0.18 ± 0.12	0.00 ± 0.44
n-pentane	*	4.64 ± 0.70	1.52 ± 1.27	0.00 ± 0.20	3.65 ± 0.69	11.91 ± 1.20	0.10 ± 0.20	1.20 ± 0.27	3.93 ± 0.61	3.77 ± 1.49	0.00 ± 0.44
isoprene	*	0.23 ± 0.04	0.00 ± 0.30	0.00 ± 0.20	0.00 ± 0.13	0.10 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.03 ± 0.05	0.18 ± 0.12	0.00 ± 0.44
t-2-Pentene		0.97 ± 0.15	0.36 ± 0.38	0.00 ± 0.20	0.75 ± 0.13	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.28 ± 0.20	0.25 ± 0.12	0.00 ± 0.10
c-2-pentene		0.49 ± 0.07	0.29 ± 0.19	0.00 ± 0.20	0.43 ± 0.08	0.93 ± 0.15	0.00 ± 0.20	0.00 ± 0.20	0.15 ± 0.10	0.13 ± 0.12	0.00 ± 0.44
2,2-dimethylbutane	*	0.37 ± 0.06	2.63 ± 0.98	0.00 ± 0.20	0.44 ± 0.07	1.16 ± 0.17	0.00 ± 0.20	0.00 ± 0.20	0.08 ± 0.08	0.16 ± 0.12	0.00 ± 0.44
cyclopentane	*	0.46 ± 0.07	0.32 ± 0.23	0.00 ± 0.20	0.46 ± 0.07	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.46 ± 0.08	0.18 ± 0.12	0.00 ± 0.44
2,3-dimethylbutane		1.19 ± 0.18	0.32 ± 0.62	0.00 ± 0.20	1.40 ± 0.09	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.37 ± 0.22	0.45 ± 0.13	0.00 ± 0.44
2-methylpentane	*	3.36 ± 0.50	1.97 ± 1.08	0.00 ± 0.20	3.97 ± 0.23	4.71 ± 0.49	0.00 ± 0.20	0.00 ± 0.20	1.39 ± 0.39	1.47 ± 0.25	0.01 ± 0.01
3-methylpentane	*	2.09 ± 0.31	0.91 ± 0.68	0.00 ± 0.20	2.61 ± 0.14	2.52 ± 0.28	0.00 ± 0.20	0.00 ± 0.20	0.81 ± 0.27	0.95 ± 0.18	0.01 ± 0.07
2-methyl-1-pentene		0.39 ± 0.06	0.22 ± 0.19	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20	0.10 ± 0.05	0.08 ± 0.11	0.00 ± 0.10
n-hexane	*	2.68 ± 0.40	0.96 ± 0.60	0.00 ± 0.20	3.46 ± 0.17	2.03 ± 0.24	0.00 ± 0.20	0.00 ± 0.20	1.95 ± 0.30	1.24 ± 0.22	0.00 ± 0.44
Methylcyclopentane	*	1.78 ± 0.27	0.62 ± 0.48	0.00 ± 0.20	2.27 ± 0.04	0.87 ± 0.15	0.00 ± 0.20	0.00 ± 0.20	1.13 ± 0.23	0.70 ± 0.17	0.04 ± 0.06
2,4-dimethylpentane	*	1.29 ± 0.19	0.36 ± 0.27	0.00 ± 0.20	1.58 ± 0.67	0.52 ± 0.14	0.00 ± 0.20	0.00 ± 0.20	0.65 ± 0.53	0.43 ± 0.13	0.01 ± 0.07
benzene	*	4.50 ± 0.68	3.19 ± 1.52	0.00 ± 0.20	2.64 ± 1.03	0.76 ± 0.14	0.00 ± 0.20	0.00 ± 0.20	1.23 ± 0.43	1.52 ± 0.38	0.00 ± 0.44
cyclohexane	*	0.90 ± 0.14	0.23 ± 0.09	0.00 ± 0.20	1.23 ± 0.02	0.20 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.57 ± 0.33	0.45 ± 0.22	0.15 ± 0.23
2-methylhexane	*	1.51 ± 0.23	0.00 ± 0.11	0.00 ± 0.20	2.10 ± 0.15	0.48 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.52 ± 0.09	0.87 ± 0.17	0.28 ± 1.22
2,3-dimethylpentane	*	1.98 ± 0.30	0.91 ± 0.37	0.00 ± 0.20	3.34 ± 0.22	0.31 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	1.17 ± 0.92	0.75 ± 0.16	0.12 ± 0.21
3-methylhexane	*	1.67 ± 0.25	2.31 ± 1.29	0.00 ± 0.20	2.38 ± 0.12	0.48 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.56 ± 0.18	0.59 ± 0.14	0.34 ± 0.45
2,2,4-trimethylpentane	*	3.04 ± 0.30	1.48 ± 1.26	0.00 ± 0.20	4.38 ± 0.69	2.13 ± 0.25	0.00 ± 0.20	0.00 ± 0.20	1.49 ± 1.60	3.92 ± 2.37	0.00 ± 0.44

[a] Profiles consisting of 100 percent isoprene (Biogenic) and 100 percent unidentified hydrocarbons (UNID) were also applied.

* Fitting species in both auto-GC and canister samples, c - fitting species in canister samples only.

Table 1 (*Continued*)
Source profiles applied in the Paso del Norte Ozone Study (volume percent of sum of 55 PAMS target species)[a] IS target species)[a]

PROFILE		Exh_J	Tu_MchHD	Exh_PBa	ME75R25P	Maga_HS	Prop_J	CNG_J	ChevFC	Zenco	COATcomp
n-heptane	*	1.62 ± 0.24	0.57 ± 0.30	0.00 ± 0.20	2.01 ± 0.10	0.37 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	1.28 ± 0.55	0.61 ± 0.15	1.57 ± 4.82
methylcyclohexane	*	0.85 ± 0.13	0.44 ± 0.27	0.00 ± 0.20	0.84 ± 0.04	0.15 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.74 ± 0.39	0.35 ± 0.15	2.61 ± 9.12
2,3,4-trimethylpentane	*	1.28 ± 0.19	0.32 ± 0.44	0.00 ± 0.20	1.87 ± 0.28	0.48 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.71 ± 0.51	0.63 ± 0.15	0.05 ± 0.10
toluene	*	10.34 ± 1.55	4.50 ± 3.64	0.00 ± 0.20	15.04 ± 0.69	1.26 ± 0.18	0.00 ± 0.20	0.00 ± 0.20	2.23 ± 0.89	19.41 ± 2.92	6.91 ± 6.86
2-methylheptane	*	0.55 ± 0.08	0.00 ± 0.21	0.00 ± 0.20	0.80 ± 0.05	0.06 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.38 ± 0.07	0.24 ± 0.12	1.36 ± 2.34
3-methylheptane	*	0.70 ± 0.11	0.44 ± 0.22	0.00 ± 0.20	0.81 ± 0.05	0.05 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.23 ± 0.06	0.23 ± 0.12	0.96 ± 1.62
n-octane	*	0.53 ± 0.08	0.31 ± 0.17	0.00 ± 0.20	0.76 ± 0.04	0.05 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.95 ± 0.45	0.34 ± 0.21	3.44 ± 5.30
ethylbenzene		2.05 ± 0.31	2.85 ± 1.98	0.00 ± 0.20	3.35 ± 0.18	0.06 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.44 ± 0.08	0.90 ± 0.18	3.82 ± 2.85
mp-xylene		6.11 ± 0.92	10.99 ± 6.84	0.00 ± 0.20	10.70 ± 0.79	0.19 ± 0.13	0.00 ± 0.20	0.00 ± 0.20	0.88 ± 0.14	2.15 ± 0.51	15.40 ± 10.58
styrene		0.46 ± 0.07	1.85 ± 0.73	0.00 ± 0.20	0.28 ± 0.02	0.02 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.26 ± 0.10	1.80 ± 0.76	0.01 ± 0.03
o-xylene		2.46 ± 0.37	3.73 ± 2.27	0.00 ± 0.20	3.95 ± 0.28	0.06 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.54 ± 0.09	0.98 ± 0.20	7.18 ± 4.36
n-nonane	*	0.19 ± 0.03	1.12 ± 0.35	0.00 ± 0.20	0.30 ± 0.07	0.02 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.74 ± 0.31	0.40 ± 0.13	4.54 ± 2.30
isopropylbenzene		0.29 ± 0.04	0.33 ± 0.17	0.00 ± 0.20	0.25 ± 0.02	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.16 ± 0.07	0.11 ± 0.11	0.63 ± 0.57
n-propylbenzene		0.58 ± 0.09	1.06 ± 0.68	0.00 ± 0.20	0.88 ± 0.05	0.01 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.13 ± 0.05	0.27 ± 0.12	1.46 ± 1.46
m-ethyltoluene		1.71 ± 0.26	4.15 ± 2.88	0.00 ± 0.20	2.75 ± 0.18	0.05 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.26 ± 0.06	0.61 ± 0.15	0.00 ± 0.44
p-ethyltoluene		0.37 ± 0.52	1.40 ± 0.73	0.00 ± 0.20	1.26 ± 0.08	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.05	0.00 ± 0.11	4.51 ± 1.66
1,3,5-trimethylbenzene		0.97 ± 0.15	2.09 ± 1.09	0.00 ± 0.20	1.43 ± 0.10	0.04 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.21 ± 0.06	0.57 ± 0.14	4.14 ± 2.64
o-ethyltoluene		0.66 ± 0.10	2.00 ± 1.12	0.00 ± 0.20	0.99 ± 0.06	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.12 ± 0.05	0.24 ± 0.12	0.00 ± 0.44
1,2,4-trimethylbenzene		2.74 ± 0.41	7.46 ± 4.64	0.00 ± 0.20	4.35 ± 0.27	0.07 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.37 ± 0.07	1.07 ± 0.21	11.13 ± 4.31
n-decane	c	0.27 ± 0.05	2.62 ± 0.64	0.00 ± 0.20	0.14 ± 0.02	0.02 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.55 ± 0.11	0.70 ± 0.30	18.12 ± 6.01
1,2,3-trimethylbenzene		0.00 ± 0.20	1.67 ± 1.04	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.10
m-diethylbenzene		0.00 ± 0.01	0.00 ± 0.11	0.00 ± 0.20	0.32 ± 0.01	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.05	0.00 ± 0.11	0.39 ± 0.42
p-diethylbenzene		0.00 ± 0.20	0.00 ± 0.11	0.00 ± 0.20	0.00 ± 0.10	0.00 ± 0.10	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.20	0.00 ± 0.10
n-undecane	c	0.17 ± 0.03	5.32 ± 1.04	0.00 ± 0.20	0.49 ± 0.03	0.02 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	0.37 ± 0.07	0.42 ± 0.13	10.81 ± 8.14
Others		11.92 ± 1.19	8.51 ± 0.85	0.00 ± 0.20	27.01 ± 1.55	0.00 ± 0.12	0.00 ± 0.20	0.00 ± 0.20	7.25 ± 1.28	8.99 ± 0.91	0.00 ± 0.10
Unidentified	c	16.11 ± 2.43	0.40 ± 0.04	0.00 ± 0.20	0.00 ± 0.13	0.00 ± 0.12	0.27 ± 0.31	0.00 ± 0.20	13.37 ± 4.25	39.41 ± 5.93	186.46 ± 22.67
NMHC		128.03 ± 12.80	108.91 ± 10.89	100.00 ± 15.00	127.01 ± 12.70	100.00 ± 10.00	100.00 ± 15.00	100.00 ± 15.00	120.63 ± 12.06	148.40 ± 14.84	286.46 ± 28.65

[a] Profiles consisting of 100 percent isoprene (Biogenic) and 100 percent unidentified hydrocarbons (UNID) were also applied.

* Fitting species in both auto-GC and canister samples, c - fitting species in canister samples only.

Table 2
Mean source contributions as percent of NMHC - 1996 Paso del Norte Ozone Study surface canister samples[a] canister samples [a]

Site [b]	Hour	No. Obs	Mean NMHC (ppbC)	Min NMHC (ppbC)	Max NMHC (ppbC)	Percent NMHC Attributed	R^2	χ^2	On-Road Vehicle Emissions	Diesel Exhaust	Liquid Gasoline	Gasoline Vapor	LPG	CNG	Surface Coating	Biogenic	Unidentified Compounds	Unexplained
M23	06	8	734 ± 136	319	1268	95.9 ± 2.7	0.97 ± 0.01	1.12 ± 0.36	66.1 ± 6.2	2.0 ± 0.8	0.0 ± 0.0	1.8 ± 1.0	14.7 ± 2.4	3.5 ± 0.9	1.1 ± 0.8	0.1 ± 0.0	6.7 ± 2.0	4.1 ± 2.7
M23	08	8	737 ± 116	459	1274	95.7 ± 1.7	0.96 ± 0.02	1.94 ± 0.85	69.2 ± 3.4	1.9 ± 0.8	0.0 ± 0.0	5.0 ± 2.6	9.8 ± 2.4	2.3 ± 0.7	2.4 ± 1.0	0.2 ± 0.1	5.0 ± 1.2	4.3 ± 1.7
M23	10	8	382 ± 34	204	512	96.8 ± 1.7	0.95 ± 0.01	1.77 ± 0.39	64.8 ± 3.6	2.8 ± 0.8	0.8 ± 0.5	4.7 ± 1.9	8.6 ± 2.4	2.3 ± 0.6	6.7 ± 2.6	0.1 ± 0.0	6.0 ± 1.3	3.2 ± 1.7
M23	12	10	342 ± 22	230	444	93.5 ± 4.2	0.95 ± 0.01	1.82 ± 0.41	56.9 ± 6.0	1.7 ± 0.5	3.2 ± 2.6	5.9 ± 1.4	6.7 ± 1.0	2.0 ± 0.3	7.7 ± 2.3	0.2 ± 0.0	9.3 ± 1.4	6.5 ± 4.2
M23	16	8	460 ± 107	193	1502	97.3 ± 0.9	0.95 ± 0.01	1.71 ± 0.33	54.3 ± 5.9	2.8 ± 0.5	7.3 ± 3.2	4.4 ± 1.4	4.4 ± 0.4	1.5 ± 0.2	4.2 ± 1.0	0.3 ± 0.1	18.1 ± 5.7	2.7 ± 0.9
MJA	06	10	1835 ± 416	826	3370	88.6 ± 4.4	0.90 ± 0.02	2.84 ± 0.76	36.3 ± 4.1	0.6 ± 0.4	0.0 ± 0.0	4.0 ± 1.2	29.0 ± 5.4	1.2 ± 0.2	4.6 ± 1.5	0.0 ± 0.0	12.8 ± 4.0	11.4 ± 4.4
MJA	08	10	855 ± 157	354	1835	86.8 ± 3.3	0.89 ± 0.02	3.53 ± 0.49	41.6 ± 2.7	0.5 ± 0.3	0.4 ± 0.3	5.0 ± 0.9	17.2 ± 2.9	3.0 ± 1.4	11.9 ± 3.6	0.0 ± 0.0	7.0 ± 2.4	13.2 ± 3.3
MJA	10	10	627 ± 103	330	1367	76.5 ± 6.8	0.82 ± 0.02	5.56 ± 0.58	30.1 ± 3.3	0.5 ± 0.5	0.0 ± 0.0	8.8 ± 1.2	9.4 ± 1.7	1.8 ± 0.3	15.8 ± 5.0	0.0 ± 0.0	10.0 ± 2.1	23.5 ± 6.8
MJA	12	10	340 ± 38	158	575	82.7 ± 3.3	0.78 ± 0.03	6.59 ± 0.75	27.3 ± 3.6	2.6 ± 1.6	1.1 ± 1.0	9.3 ± 1.0	6.4 ± 0.9	1.9 ± 0.2	21.8 ± 3.1	0.0 ± 0.0	12.3 ± 1.9	17.3 ± 3.3
MJA	16	10	498 ± 48	248	812	73.3 ± 4.4	0.75 ± 0.03	7.98 ± 0.78	25.2 ± 3.6	1.6 ± 0.7	0.0 ± 0.0	7.4 ± 0.9	4.8 ± 0.4	1.6 ± 0.3	8.3 ± 1.2	0.1 ± 0.1	24.3 ± 2.5	26.7 ± 4.4
TEE	10	5	219 ± 21	134	318	88.4 ± 1.6	0.93 ± 0.01	1.97 ± 0.32	22.5 ± 1.4	1.8 ± 0.6	8.0 ± 1.1	7.4 ± 3.2	3.5 ± 1.0	4.0 ± 1.1	5.0 ± 1.3	0.3 ± 0.1	36.1 ± 3.9	11.6 ± 1.6
TEE	12	4	187 ± 29	69	314	82.7 ± 1.9	0.84 ± 0.03	3.61 ± 0.71	22.5 ± 2.1	4.5 ± 1.3	3.3 ± 1.1	7.3 ± 2.8	3.9 ± 0.7	4.0 ± 0.6	4.2 ± 0.9	0.3 ± 0.1	32.7 ± 3.6	17.3 ± 1.9
TED	06	9	608 ± 127	304	1159	95.2 ± 3.0	0.97 ± 0.00	0.91 ± 0.15	62.6 ± 6.3	0.4 ± 0.3	2.8 ± 1.4	2.0 ± 1.3	5.4 ± 2.9	3.4 ± 0.8	2.4 ± 0.6	0.1 ± 0.0	16.2 ± 4.8	4.8 ± 3.0
TED	08	10	560 ± 92	149	1062	98.3 ± 1.7	0.97 ± 0.01	1.06 ± 0.18	68.2 ± 5.2	1.4 ± 0.8	3.5 ± 1.9	2.0 ± 0.8	3.5 ± 1.3	2.9 ± 0.5	2.4 ± 0.5	0.1 ± 0.0	14.2 ± 3.7	1.7 ± 1.7
TED	10	8	356 ± 48	178	604	98.6 ± 0.7	0.97 ± 0.01	1.03 ± 0.31	70.3 ± 3.6	0.4 ± 0.2	4.2 ± 1.5	2.1 ± 0.9	3.7 ± 1.3	3.5 ± 0.8	3.9 ± 0.9	0.1 ± 0.0	10.6 ± 2.3	1.4 ± 0.7
TED	12	8	343 ± 42	170	555	98.3 ± 1.1	0.97 ± 0.01	1.26 ± 0.46	65.3 ± 2.9	0.1 ± 0.0	4.5 ± 1.9	3.2 ± 0.7	3.7 ± 2.0	3.2 ± 0.6	2.5 ± 0.9	0.1 ± 0.0	15.7 ± 1.3	1.7 ± 1.1
TED	16	9	305 ± 26	139	435	96.7 ± 0.4	0.99 ± 0.00	0.46 ± 0.04	71.6 ± 2.1	0.8 ± 0.3	5.4 ± 0.9	1.3 ± 0.4	0.7 ± 0.2	3.0 ± 0.3	0.6 ± 0.2	0.2 ± 0.0	13.3 ± 1.3	3.3 ± 0.4
DYR	10	4	165 ± 19	101	217	81.5 ± 3.7	0.84 ± 0.03	3.79 ± 1.06	12.5 ± 3.5	0.0 ± 0.0	12.0 ± 2.5	6.1 ± 1.7	3.2 ± 1.1	5.0 ± 1.2	9.3 ± 2.9	0.1 ± 0.1	33.3 ± 3.8	18.5 ± 3.7
DYR	12	5	146 ± 24	79	288	86.0 ± 1.6	0.85 ± 0.02	2.37 ± 0.65	9.8 ± 2.3	2.4 ± 0.7	4.7 ± 1.0	2.5 ± 0.4	4.2 ± 1.1	4.7 ± 1.0	5.9 ± 2.3	0.1 ± 0.0	51.6 ± 4.4	14.0 ± 1.6
FKM	06	3	197 ± 21	141	243	96.2 ± 0.6	0.94 ± 0.02	1.46 ± 0.39	50.5 ± 8.5	0.2 ± 0.2	0.6 ± 0.4	4.4 ± 1.5	7.2 ± 1.9	6.1 ± 2.4	2.6 ± 0.3	0.0 ± 0.0	24.6 ± 3.2	3.8 ± 0.6
FKM	08	5	179 ± 17	128	249	95.3 ± 0.8	0.94 ± 0.01	1.35 ± 0.29	40.1 ± 8.1	1.5 ± 0.6	2.2 ± 0.5	2.6 ± 1.1	3.6 ± 1.1	5.6 ± 1.8	3.6 ± 0.7	0.2 ± 0.0	35.9 ± 5.6	4.7 ± 0.8
JPS	06	3	1290 ± 251	686	1914	97.8 ± 0.5	0.99 ± 0.00	0.45 ± 0.06	61.3 ± 0.4	0.6 ± 0.3	1.0 ± 0.7	0.6 ± 0.4	23.6 ± 0.9	2.7 ± 0.2	1.3 ± 0.5	0.0 ± 0.0	6.7 ± 1.2	2.2 ± 0.5
JPS	22	4	2148 ± 261	773	3693	101.7 ± 0.3	0.99 ± 0.00	0.47 ± 0.01	61.0 ± 1.3	0.3 ± 0.1	4.1 ± 0.4	5.5 ± 0.6	21.4 ± 1.5	1.3 ± 0.1	1.6 ± 0.1	0.0 ± 0.0	6.5 ± 0.6	-1.7 ± 0.3
NPS	06	5	329 ± 74	178	644	100.5 ± 1.2	0.97 ± 0.01	0.93 ± 0.21	48.2 ± 4.1	0.5 ± 0.2	6.0 ± 4.9	2.3 ± 1.5	20.1 ± 6.9	7.8 ± 2.1	2.1 ± 0.3	0.2 ± 0.0	13.3 ± 3.0	-0.5 ± 1.2
NPS	08	5	217 ± 41	98	406	101.8 ± 0.6	0.96 ± 0.00	1.09 ± 0.18	46.3 ± 6.0	1.9 ± 0.7	8.1 ± 2.8	4.8 ± 1.9	14.5 ± 3.2	5.6 ± 1.6	2.9 ± 0.7	0.2 ± 0.0	17.5 ± 3.7	-1.8 ± 0.6
TRF	06	6	166 ± 26	47	234	95.5 ± 4.0	0.91 ± 0.02	1.88 ± 0.28	37.1 ± 6.4	8.3 ± 2.9	11.3 ± 6.2	0.8 ± 0.5	12.6 ± 3.7	7.1 ± 3.0	0.5 ± 0.5	0.0 ± 0.0	17.7 ± 10.0	4.5 ± 4.0
TRF	08	6	126 ± 30	39	269	94.3 ± 3.9	0.91 ± 0.03	1.66 ± 0.42	40.1 ± 5.1	7.1 ± 1.6	7.1 ± 2.0	8.9 ± 4.4	9.5 ± 1.1	8.0 ± 2.5	0.5 ± 0.2	0.0 ± 0.0	13.2 ± 4.4	5.7 ± 3.9
TRF	10	6	97 ± 14	54	170	94.2 ± 2.3	0.91 ± 0.02	1.68 ± 0.27	37.8 ± 7.9	10.0 ± 1.6	6.9 ± 2.5	12.1 ± 2.1	5.3 ± 0.6	6.7 ± 1.4	0.5 ± 0.2	0.0 ± 0.0	14.8 ± 3.7	5.8 ± 2.3
TRF	12	6	109 ± 24	40	264	92.2 ± 2.8	0.88 ± 0.01	2.74 ± 0.38	18.9 ± 4.0	9.2 ± 1.6	16.7 ± 2.9	18.4 ± 2.9	3.5 ± 0.4	7.7 ± 1.3	0.4 ± 0.3	0.1 ± 0.1	17.2 ± 5.5	7.8 ± 2.8
TRF	16	8	99 ± 10	53	162	91.9 ± 2.1	0.90 ± 0.01	2.20 ± 0.40	26.0 ± 4.6	9.0 ± 1.7	9.8 ± 1.8	12.2 ± 1.4	3.5 ± 0.4	6.7 ± 1.3	4.2 ± 1.7	0.2 ± 0.1	20.3 ± 4.7	8.1 ± 2.1
TRF	20	4	63 ± 5	41	91	84.5 ± 3.6	0.82 ± 0.02	2.27 ± 0.22	23.7 ± 5.6	11.5 ± 1.0	13.4 ± 3.2	0.5 ± 0.2	6.0 ± 0.4	13.4 ± 0.8	2.4 ± 0.9	0.1 ± 0.0	13.4 ± 1.7	15.5 ± 3.6
WIN	06	6	644 ± 132	232	973	101.1 ± 2.0	0.97 ± 0.00	1.09 ± 0.20	60.9 ± 2.1	0.5 ± 0.4	15.1 ± 4.7	0.4 ± 0.3	12.4 ± 4.2	4.7 ± 1.2	0.2 ± 0.1	0.1 ± 0.0	6.7 ± 3.4	-1.1 ± 2.0
WIN	08	7	298 ± 70	105	623	103.9 ± 1.7	0.95 ± 0.01	1.54 ± 0.31	53.9 ± 4.2	1.9 ± 0.7	12.7 ± 3.8	1.1 ± 0.5	18.9 ± 2.5	5.2 ± 1.2	0.3 ± 0.2	0.2 ± 0.0	9.8 ± 5.4	-3.9 ± 1.7
WIN	10	7	137 ± 38	37	388	100.2 ± 2.3	0.87 ± 0.04	2.55 ± 0.75	48.7 ± 7.0	4.9 ± 2.0	8.8 ± 3.4	1.9 ± 0.8	12.0 ± 1.8	8.0 ± 1.3	0.7 ± 0.3	0.4 ± 0.1	14.8 ± 3.1	-0.2 ± 2.3
WIN	12	8	95 ± 22	39	261	96.3 ± 2.3	0.86 ± 0.02	2.02 ± 0.26	30.0 ± 2.5	7.4 ± 1.6	12.4 ± 3.3	0.7 ± 0.3	7.2 ± 0.9	10.5 ± 2.1	1.5 ± 0.6	1.2 ± 0.5	25.6 ± 5.0	3.7 ± 2.3
WIN	16	5	79 ± 9	43	129	94.1 ± 1.5	0.71 ± 0.05	4.00 ± 0.64	23.9 ± 6.7	12.4 ± 1.8	15.1 ± 2.6	0.1 ± 0.0	7.4 ± 1.3	9.1 ± 1.8	0.4 ± 0.1	0.7 ± 0.1	25.1 ± 6.4	5.9 ± 1.5

[a] Uncertainities are standard errors.

[b] Site abbreviations: 20/30 Club (M23), Advance Transformer (MJA), Ascarate Park (TEE), Campbell (TED), Dyer Street (DYR), Franklin Mountain (FKM), Cuidad Juárez Police Station (JPS), Sunland Park (NSP), Turf Road (TRF), and Winn Road (WIN).

3. Results

3.1. Source apportionment results

Table 2 shows the 2-h average contributions (in percent) for the canister samples from the various study sites. The major contributor to ambient NMHC in the Paso del Norte area during the study period was on-road vehicle emissions. Depending upon time and location, liquid gasoline, gasoline vapor, diesel exhaust, LPG, CNG, and unidentified compounds (i.e. from the profile unid) were also significant contributors to ambient NMHC. Model performance parameters were generally good for urban samples with average *r*-squares greater than 0.95, chi-squares less than 2 and total contributions of 95–100%. Samples from the two downwind sites (Turf Road and Winn Road) gave average *r*-squares between 0.87 and 0.9, chi-squares from 1 to near 3, and total assigned contributions between 85 and 104% of NMHC.

Gasoline vehicle exhaust accounted for one-half to two-thirds of NMHC in central Ciudad Juárez (20/30 Club) and El Paso (Campbell) with the highest contributions during the morning and af-

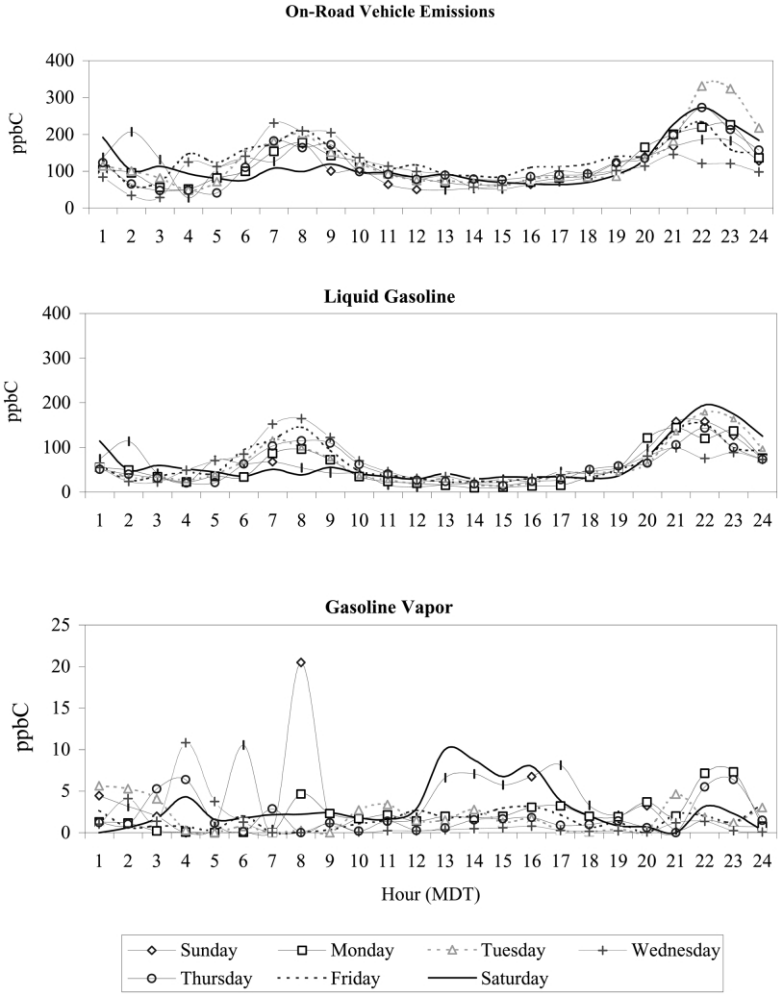

Fig. 3. Mean diurnal variations (MDT) in hydrocarbon source contributions (ppbC) at Chamizal Park by day of the week during summer 1996.

Table 3
Mean hourly source contributions as percent of NMHC for auto-GC samples from Chamizal Park (6/1/96 to 9/30/96)[a] /1/96 to 9/30/96) [a]

Hour (MDT)	No. Obs	Mean NMHC (ppbC)	Minimum NMHC (ppbC)	Maximum NMHC (ppbC)	Percent NMHC Attributed	R^2	χ^2	On-Road Vehicle Emissions	Diesel Exhaust	Liquid Gasoline	Gasoline Vapor	LPG	CNG	Biogenic	Unexplained
0	108	241.5 ± 29.6	10	2186	98.6 ± 0.9	0.930 ± 0.002	1.60 ± 0.10	55.1 ± 1.3	1.2 ± 0.4	27.7 ± 1.0	1.3 ± 0.3	6.6 ± 0.6	6.8 ± 0.4	0.0 ± 0.0	1.4 ± 0.9
1	51	196.3 ± 43.6	20	2133	99.3 ± 1.0	0.929 ± 0.004	1.47 ± 0.14	53.9 ± 1.9	1.0 ± 0.3	25.8 ± 1.4	1.3 ± 0.4	8.3 ± 1.0	9.1 ± 0.8	0.0 ± 0.0	0.7 ± 1.0
2	51	147.8 ± 19.9	20	642	99.1 ± 1.1	0.926 ± 0.004	1.54 ± 0.16	52.8 ± 1.7	1.6 ± 0.4	25.8 ± 1.3	1.4 ± 0.4	7.6 ± 0.9	9.9 ± 0.8	0.0 ± 0.0	0.9 ± 1.1
3	49	154.8 ± 26.0	17	855	97.3 ± 1.0	0.916 ± 0.005	1.71 ± 0.17	53.2 ± 2.0	1.9 ± 0.5	23.2 ± 1.5	2.0 ± 1.0	7.6 ± 1.1	9.3 ± 0.7	0.0 ± 0.0	2.7 ± 1.0
4	55	168.2 ± 20.7	15	614	95.9 ± 1.4	0.924 ± 0.004	1.63 ± 0.14	52.5 ± 1.6	1.1 ± 0.4	25.0 ± 1.2	0.7 ± 0.2	7.5 ± 1.0	9.1 ± 0.7	0.0 ± 0.0	4.1 ± 1.4
5	93	237.3 ± 21.6	29	1046	94.0 ± 0.8	0.917 ± 0.003	2.02 ± 0.13	53.8 ± 1.2	1.6 ± 0.3	25.4 ± 1.0	0.6 ± 0.2	5.8 ± 0.7	6.8 ± 0.4	0.1 ± 0.0	6.0 ± 0.8
6	101	334.3 ± 25.9	39	1154	90.4 ± 0.7	0.908 ± 0.003	2.53 ± 0.12	50.3 ± 1.2	0.6 ± 0.2	28.8 ± 0.9	0.3 ± 0.1	5.5 ± 0.6	4.8 ± 0.3	0.1 ± 0.0	9.6 ± 0.7
7	102	351.4 ± 28.3	24	1895	90.2 ± 0.8	0.903 ± 0.004	2.78 ± 0.14	52.0 ± 1.3	0.5 ± 0.2	27.9 ± 1.0	0.5 ± 0.2	5.0 ± 0.6	4.2 ± 0.3	0.1 ± 0.0	9.8 ± 0.8
8	101	280.9 ± 23.1	50	946	94.3 ± 0.8	0.910 ± 0.003	2.47 ± 0.14	57.3 ± 1.3	0.5 ± 0.2	26.3 ± 0.9	0.5 ± 0.2	5.2 ± 0.5	4.4 ± 0.3	0.1 ± 0.0	5.7 ± 0.8
9	102	192.6 ± 15.2	34	1098	97.6 ± 0.8	0.918 ± 0.003	2.02 ± 0.12	62.5 ± 1.2	0.7 ± 0.2	23.6 ± 0.9	0.8 ± 0.3	5.3 ± 0.5	4.5 ± 0.3	0.1 ± 0.0	2.4 ± 0.8
10	97	143.5 ± 9.1	30	608	101.5 ± 1.0	0.923 ± 0.003	1.70 ± 0.09	67.8 ± 1.4	1.0 ± 0.3	21.1 ± 1.1	1.1 ± 0.2	5.6 ± 0.6	4.8 ± 0.3	0.1 ± 0.0	-1.5 ± 1.0
11	95	120.0 ± 7.4	24	379	104.2 ± 1.1	0.929 ± 0.002	1.43 ± 0.07	72.1 ± 1.5	0.7 ± 0.2	20.1 ± 1.1	1.2 ± 0.3	5.3 ± 0.5	4.7 ± 0.3	0.1 ± 0.0	-4.2 ± 1.1
12	96	120.7 ± 7.2	24	351	106.0 ± 1.6	0.931 ± 0.004	1.43 ± 0.09	71.3 ± 1.9	0.7 ± 0.2	22.0 ± 1.4	3.0 ± 0.5	4.7 ± 0.5	4.3 ± 0.2	0.1 ± 0.0	-6.0 ± 1.6
13	97	124.5 ± 26.1	19	2589	105.4 ± 1.9	0.929 ± 0.004	1.36 ± 0.09	72.3 ± 2.0	0.8 ± 0.2	19.9 ± 1.3	3.5 ± 0.6	4.5 ± 0.5	4.2 ± 0.2	0.1 ± 0.0	-5.4 ± 1.9
14	95	95.0 ± 5.7	19	269	108.4 ± 1.1	0.934 ± 0.001	1.23 ± 0.06	74.7 ± 1.8	0.7 ± 0.2	21.0 ± 1.5	3.3 ± 0.5	4.2 ± 0.4	4.5 ± 0.3	0.1 ± 0.0	-8.4 ± 1.1
15	98	112.0 ± 6.4	21	295	106.6 ± 1.1	0.934 ± 0.002	1.34 ± 0.06	73.1 ± 1.8	0.5 ± 0.2	22.2 ± 1.5	3.8 ± 0.6	3.2 ± 0.3	3.8 ± 0.2	0.1 ± 0.0	-6.6 ± 1.1
16	101	126.2 ± 7.8	24	486	105.8 ± 1.0	0.930 ± 0.002	1.51 ± 0.08	72.7 ± 1.9	0.4 ± 0.1	24.5 ± 1.6	2.6 ± 0.5	2.3 ± 0.3	3.4 ± 0.2	0.1 ± 0.0	-5.8 ± 1.0
17	108	139.0 ± 8.1	28	477	103.4 ± 1.1	0.930 ± 0.002	1.55 ± 0.07	69.4 ± 1.8	0.7 ± 0.2	27.0 ± 1.4	1.1 ± 0.2	1.8 ± 0.2	3.2 ± 0.2	0.1 ± 0.0	-3.4 ± 1.1
18	109	172.3 ± 10.3	24	795	101.6 ± 1.0	0.928 ± 0.002	1.76 ± 0.08	67.0 ± 1.8	0.3 ± 0.1	28.4 ± 1.3	0.7 ± 0.2	2.0 ± 0.2	3.0 ± 0.2	0.1 ± 0.0	-1.6 ± 1.0
19	106	252.4 ± 17.6	50	1323	96.5 ± 0.9	0.921 ± 0.003	2.19 ± 0.11	58.0 ± 1.5	0.1 ± 0.1	32.7 ± 1.0	0.5 ± 0.1	2.4 ± 0.2	2.7 ± 0.2	0.1 ± 0.0	3.5 ± 0.9
20	111	387.1 ± 29.6	27	1372	93.9 ± 0.7	0.915 ± 0.003	2.51 ± 0.13	53.2 ± 1.3	0.4 ± 0.2	33.7 ± 0.9	0.3 ± 0.1	3.5 ± 0.3	2.8 ± 0.2	0.1 ± 0.0	6.1 ± 0.7
21	115	469.6 ± 44.7	25	3035	93.2 ± 0.8	0.912 ± 0.003	2.55 ± 0.13	53.2 ± 1.2	0.5 ± 0.2	31.3 ± 0.9	0.7 ± 0.2	4.3 ± 0.4	3.2 ± 0.2	0.1 ± 0.0	6.8 ± 0.8
22	116	416.0 ± 47.2	25	3165	94.0 ± 0.7	0.919 ± 0.003	2.22 ± 0.12	53.7 ± 1.2	0.5 ± 0.2	30.7 ± 0.9	0.7 ± 0.2	4.4 ± 0.4	3.9 ± 0.2	0.1 ± 0.0	6.0 ± 0.7
23	115	295.1 ± 30.1	20	1881	95.5 ± 0.8	0.924 ± 0.003	1.95 ± 0.11	53.7 ± 1.1	0.6 ± 0.2	30.0 ± 0.9	0.5 ± 0.2	5.7 ± 0.5	5.0 ± 0.3	0.0 ± 0.0	4.5 ± 0.8

[a] Uncertainities are standard errors.

ternoon commute periods. Emissions from diesel exhaust were 2–3% of NMHC at 20/30 Club and $<2\%$ at Campbell. The average sum of liquid gasoline and gasoline vapor increased during the day at 20/30 Club from 2% at 06.00 h to approximately 12% at 16.00 h. The contribution of gasoline to NMHC at Campbell ranged from 5 to 7%. LPG was also a larger contributor in Ciudad Juárez than in El Paso (4–15% at 20/30 Club vs. 1–3% at Campbell). Surface coatings contributed 1–8% of NMHC at 20/30 Club and 1–4% at Campbell. The balance of NMHC was associated with unidentified compounds. The unidentified and/or unexplained fractions were greatest in rural locations and tended to increase in the afternoons at most sites. These diurnal differences in the fraction of unidentified compounds between source and receptor areas suggest that a portion of the unidentified NMHC may have been associated with products of photochemical reactions. Biogenic emissions were not significant sources of ambient NMHC in the Paso del Norte study area.

The contributions of diesel exhaust were also higher at Turf Road and Winn Road than in the central urban sites, accounting for 7–12% of NMHC at Turf Road and 1–12% at Winn Road. Liquid gasoline and gasoline vapors also accounted for a larger fraction of NMHC (12–30%) at these downwind sites. The hydrocarbon apportionments at the other sites reflected characteristics of both urban source and downwind receptor areas.

Table 3 shows the average hourly source contributions (in percent) for the auto-GC samples from Chamizal Park and Fig. 3 shows the average diurnal variations by day of the week. Based on an average of all samples, the major contributors to NMHC at Chamizal Park were gasoline vehicle exhaust (61% based on the Ciudad Juárez rush hour traffic profile) and liquid gasoline (26%). Diesel exhaust (1%), natural gas (5%), liquefied petroleum gas (5%), and gasoline vapors (1%) were minor contributors to NMHC. Biogenic emissions were not significant. The gasoline contribution at Chamizal Park was greater than twice the contributions at the 20/30 Club and Campbell sites.

4. Discussion

The on-road vehicle profile that is used in this study was derived from roadside measurements that may include evaporative emissions of gasoline liquid and vapors. Furthermore, roadside measurements in Ciudad Juárez may not have been representative of the fleet-average vehicle exhaust profile in El Paso. Previous studies have shown that the source attribution between tailpipe and evaporative emissions from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley et al., 1992; Fujita et al., 1994; Pierson et al., 1999). This is because tailpipe emissions are a mixture of hydrocarbons produced during combustion along with unburned gasoline resulting from incomplete combustion. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). The profile for gasoline headspace vapor was taken to represent fuel tank vapor losses (e.g. migration of fuel vapor from the canister). If vehicles in Ciudad Juárez emitted a greater proportion of unburned gasoline in their exhaust than vehicles in El Paso, the use of profile Exh–J in the apportionment of ambient hydrocarbons in El Paso would have resulted in an underestimation of vehicle exhaust and overestimation of liquid gasoline. The similar diurnal variations shown in Fig. 3 for on-road vehicle emissions and liquid gasoline source contributions support this conclusion. The sum of the two sources put the upper limit for tailpipe contributions at 60–70% of NMHC.

Initial sensitivity tests indicated that contributions of industrial sources could not be determined from the industrial source profiles that were developed for this study. The Zenco and Chevron refinery profiles were based upon ambient samples taken at the downwind edge of the facility. These samples consist primarily of aged emissions in the regional background and local vehicular emissions. Consequently, they were collinear with the on-road vehicle emissions. Be-

cause unreactive alkanes such as ethane and propane were the most abundant species in regional background, the industrial source profiles were also collinear with LPG and CNG.

The source attributions of the hourly auto-GC data enhances our understanding of the temporal variability in source contributions. Fig. 3 shows the diurnal variations of the absolute source contributions (ppbC) for on-road vehicle emission, liquid gasoline, and gasoline vapor by day of the week. Peaks in vehicle emissions generally corresponded to morning and evening periods. Weekends were a notable exception to this pattern. The average contributions were significantly lower during weekend mornings due to reduced traffic. These patterns provide some confidence in the proper apportionment of vehicle emissions.

The diurnal and day-of-the-week patterns in the liquid gasoline contributions were essentially identical to the corresponding patterns for motor vehicle emissions. These patterns support the conclusion that a large fraction of the liquid gasoline contribution was associated with tailpipe emissions rather than evaporative emissions from either vehicle or industrial sources.

In contrast to tailpipe contributions, the average diurnal patterns of gasoline vapor contributions showed no consistent peaks during the commute periods. The contributions of gasoline vapor showed occasional spikes during the night. The average gasoline vapor contributions showed an overall trend of increasing contributions over the course of the day. This trend was all the more significant considering the counter trend of increased mixing during the afternoon. This was consistent with the diurnal patterns of ambient isopentane concentrations, which was a major component in gasoline vapor profile, and diurnal temperature variations.

5. Conclusion

On-road vehicle emissions accounted for one-half to two-thirds of NMHC in central Ciudad Juárez (20/30 Club) and El Paso (Campbell) with the highest contributions occurring during the morning and afternoon commute periods. Emissions from diesel exhaust were 2–3% of NMHC at 20/30 Club and $< 2\%$ at Campbell. The average sum of liquid gasoline and gasoline vapor increased during the day at 20/30 Club from 2% at 06.00 h to approximately 12% at 16.00 h. The contribution of gasoline to NMHC was 5–7% at Campbell. LPG and CNG were also larger contributors in Ciudad Juárez than in El Paso (6–18% at 20/30 Club vs. 4–9% at Campbell). This source contribution may have been associated with unreactive alkanes that made up a significant fraction of NMHC in the regional background. Surface coatings contributed 1–8% of NMHC at 20/30 Club and 1–4% at Campbell. The balance of NMHC was unidentified or unexplained. This fraction increased during the afternoon sampling periods at downwind sites. In central El Paso (Chamizal Park), diurnal and day-of-the-week patterns in the liquid gasoline contributions were essentially identical to the corresponding patterns for motor vehicle exhaust. These patterns suggest that a large fraction of the liquid gasoline contribution was associated with tailpipe emissions rather than evaporative emissions from either vehicle or industrial sources. The sum of the two sources put the upper limit for tailpipe contributions at 60–70% of NMHC at the 20/30 Club and Campbell.

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